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(54) Title: OLIGOMERIC DISPERSANT

(57) Abstract: A cementitious formulation comprising a cement and an oligomeric dispersant is provided. The dispersant is a reaction product of two or three moieties. The first moiety (A) is a nonpolymeric, functional moiety that adsorbs on to a particle, and wherein one or more A moieties together contain at least two residues to provide attachment of the dispersant on to a particle to be dispersed. The second required moiety (C) is a linear or branched water soluble, nonionic polymer that provides the dispersing capability. A third moiety (B), if present, is a nonpolymeric moiety disposed between the first and second moiety, to connect the first and second moieties. A method is provided for dispersing a cementitious formulation comprising a cement in water, including providing in said cementitious formulation the above oligomeric dispersant. A combination of any cement dispersant with an oligomeric dispersant wherein at least one A moiety is blocked is also provided in a cementitious formulation and in a method of making such cementitious formulation.

OLIGOMERIC DISPERSANT

FIELD OF THE INVENTION

5 The present invention is directed to an oligomeric dispersant. More particularly, the present invention is directed to an oligomeric dispersant for cementitious particles. Specifically, the present invention is directed to a reaction product of a moiety that adsorbs on to a particle to be dispersed, a moiety that provides the dispersing capability, and an optional moiety that is disposed between the other
10 moieties to provide connections between the other moieties.

BACKGROUND OF THE INVENTION

 A cementitious mixture refers to pastes, mortars, and concrete compositions
15 comprising a hydraulic cement binder. Pastes are defined as mixtures composed of a hydraulic cement binder, either alone or in combination with pozzolans such as fly ash, silica fume, or blast furnace slag, and water. Mortars are defined as pastes that additionally include fine aggregate. Concretes additionally include coarse aggregate. These compositions may additionally include other admixtures such as set retarders, set
20 accelerators, defoaming agents, air-entraining or air-detraining agents, corrosion inhibitors, water-reducing agents, pigments, and any other admixture that does not adversely affect the advantageous results obtained by the present invention.

 Dispersants are substances that improve the flow characteristics of a cement
25 slurry by breaking up cement agglomerates and freeing the water, thus giving slurries of lower viscosity and allowing desirable flow conditions to be obtained at lower pump pressures. (See, for example, V.S. Ramachandran, Concrete Admixtures Handbook: Properties, Science, and Technology, Noyes Publications (Second Edition, 1995)).

30 Dispersants have been used in the construction industry to disperse cementitious mixtures. Dispersants such as sulfonated melamine formaldehyde condensate (SMF), sulfonated naphthalene formaldehyde condensate (BNS), and lignosulfonates are

commonly used as dispersants. However, in order to achieve a desired level of concrete workability or water reduction, more of such compounds than is desirable need be added. In addition, these materials do not achieve full range (Type A to Type F) water-reducing capability, as defined in ASTM C494. For example, lignosulfonates achieve only a low
5 to mid-range (5-12%) water reduction.

Dispersants are a necessary component in high strength and high durability concretes. Due to the requirement for the use of low amounts of water in high performance concretes, high dispersant amounts are sometimes necessary to achieve
10 workable concretes. High BNS levels can lead to undesirable retardation of set and may not provide the required workability retention over time.

It is desirable to provide a material that is several times more efficient as a cement or concrete dispersant than the traditional materials such as lignosulfonates, BNS
15 and SMF. Improving efficiency reduces the amount of material required to achieve a desired level of concrete workability or water reduction. With respect to the presently-used dispersants, lignosulfonates, BNS and SMF, it is also desirable to improve slump retention while maintaining normal setting characteristics. Providing a dispersant with full range (Type A to F) water-reducing capability is also a desirable characteristic.

20

One improvement in the prior art was the introduction of polycarboxylate dispersants. Polycarboxylate dispersants are structured with a polymeric backbone, such as a carbon chain backbone, with pendant moieties. The pendant moieties provide the dispersing capabilities of the molecule. For example, polyacrylic acid has
25 carboxylic groups attached to the backbone. In addition, side chain moieties such as polyoxyalkylenes can be attached to the carboxylic groups to provide further dispersing capabilities. These dispersants operate by surrounding a particle to be dispersed, and then repulsion forces between each polymer chain keeps the particles apart and the dispersion more fluid.

30

It is an object of the invention to provide oligomeric dispersants for dispersing cementitious particles, wherein the dispersant adsorbs on to the particle to be dispersed.

SUMMARY OF THE INVENTION

The present invention provides a cementitious formulation comprising a hydraulic cement and a dispersant comprising a reaction product of component A, optionally component B, and component C;

wherein each component A is independently a nonpolymeric, functional moiety capable of adsorbing on to a cementitious particle, and contains at least one residue derived from a first component selected from the group consisting of phosphates, phosphonates, phosphinates, hypophosphites, sulfates, sulfonates, sulfinates, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid esters, alcohols, carbohydrates, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, salts of any of the preceding moieties, and mixtures thereof;

wherein component B is an optional moiety, where if present, each component B is independently a nonpolymeric moiety that is disposed between the component A moiety and the component C moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, alicyclic hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, aryl, phosphoester, nitrogen-containing compounds, and mixtures thereof; and

wherein component C is at least one moiety that is a linear or branched water-soluble nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof;

wherein if the A moiety contains any phosphate, phosphonate, phosphinate, or hypophosphite residue the molecule is further characterized by at least one of the following:

- 5 A) the molecule has a structure selected from the group consisting of:
- (i) A_x-C , (ii) A_x-C-A_x , (iii) $C-A_x-C$,
 (iv) $(C)_z-B-A_x-B-(C)_z$, (v) $(A_x)_y-B-C-B-(A_x)_y$, and mixtures thereof;
- B) on any given A moiety there is more than one residue selected from the group consisting of phosphates, phosphonates, phosphinates, or hypophosphites; or salts thereof;
- 10 C) the molecule has a structure of $(A_x)_y-B-(C)_z$ with the proviso that the B moiety and the A moiety are not bound to each other through an alkylidene amine linkage;
- D) the C moiety is selected from the group consisting of poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine),
15 monoaryloxy poly(oxyalkylene amine), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof;

 wherein x is an integer from 1 to 3 and represents the number of independent A moieties, y is an integer from 1 to 3 and represents the number of independent chains of A moieties, and z is an integer from 1 to 3 and
20 represents the number of independent C moieties.

The present invention further provides a method of dispersing a cementitious formulation comprising a hydraulic cement in water, comprising providing in said
25 cementitious formulation a dispersant as hereinabove described and mixing said cementitious formulation.

DETAILED DESCRIPTION OF THE INVENTION

30 The oligomeric cement dispersant of the present invention does not have a polymeric backbone with pendant groups as do dispersants of the prior art. Rather, the oligomeric cement dispersant has a moiety that will adsorb on to the particle to be

dispersed by means of one or more residues attached to an adsorbing moiety of absolute molecular weight. The adsorbing moiety acts as an "anchor" to hold the dispersant on to the particle to be dispersed.

- 5 One embodiment of the present invention is a composition of matter adapted for dispersing cementitious particles in water, comprising a reaction product of component A, optionally component B, and component C.

Each component A is independently a nonpolymeric, functional moiety that
10 adsorbs on to a particle, and contains at least one residue derived from a component selected from the group consisting of phosphates, phosphonates, phosphinates, hypophosphites, sulfates, sulfonates, sulfinates, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid
15 esters, alcohols, carbohydrates, derivatives of carbohydrates, salts of any of the preceding moieties, and mixtures thereof. Derivatives of carbohydrates include, but are not limited to, phosphate esters of sugars, borate esters of sugars, and sulfate esters of sugars.

20 The salt of moiety A is selected from the group consisting of lithium, sodium, potassium, calcium, magnesium, aluminum, iron, ammonia, amines, and mixtures thereof. The term amines is meant to include primary, secondary, and tertiary amines, including, but not limited to, substituted amines such as triethanolamine or morpholine.

25 Molecules satisfying the requirement of the A moiety include, but are not limited to, multihydroxy compounds, such as sugars, sugar acids, lactones of sugar acids, sugar alcohols, tris(hydroxymethyl) aminomethane, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, alkyl phosphates, substituted alkyl phosphates, alkyl phosphonates, substituted alkyl phosphonates, alkyl phosphinates,
30 substituted alkyl phosphinates, aryl boronic acids, esters of aryl boronic acids, aryl dioxaborolanes, triaryl boroxines, trialkoxyboroxines, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, hydroxy carboxylic acids, non-polymeric

polycarboxylic acids, and mixtures thereof. The alkyl groups in the above molecules are generally C₁ to C₆ groups, the aryl groups in the above molecules are generally C₆ to C₁₀ groups, and the acyl groups in the above molecules are generally C₁ to C₆ groups. The substituted alkyls can be hydroxyalkyls or carboxyalkyls.

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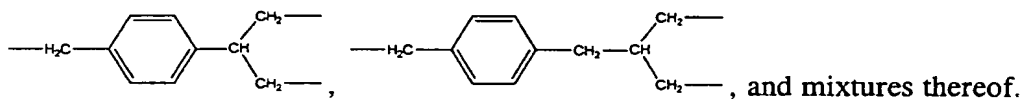
Illustrative examples of molecules used to construct the A moiety include, but are not limited to, 2-carboxyethyl phosphonic acid, sulfosuccinic acid, citric acid, 2-phosphono-1,2,4-butane tricarboxylic acid, glucuronic acid, ethylenediaminetetraacetic acid, gluconic acid, cyclohexane hexacarboxylic acid, mellitic acid, saccharic acid, 10 mucic acid, diethylenetriamine pentaacetic acid, glucoheptonic acid, glucoheptonic lactone, lactobionic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 2-(4'-carboxyphenyl)-1,3,2-dioxaborolane, triphenyl boroxine, 4-carboxyphenyl boronic acid, 4-formylphenyl boronic acid, 2-(4'-formylphenyl)-1,3,2-dioxaborolane, amino propyl trimethoxysilane, aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxy 15 silane, 3-glycidoxypropyltriethoxysilane, 3-(triethoxysilyl)propyl isocyanate, 3-(trimethoxysilyl)propyl isocyanate, glucooctanoic- γ -lactone, glucose, leucrose, diaminopropane-N,N,N',N'-tetraacetic acid, aconitic acid, isocitric acid, 1,2,3,4-butanetetracarboxylic acid, nitrilotriacetic acid, tricarballic acid, N-(phosphonomethyl)iminodiacetic acid, 3-[[tris(hydroxymethyl)methyl] amino]-1- 20 propanesulfonic acid, 2-[[tris(hydroxymethyl)methyl] amino]-1-ethanesulfonic acid, 3-[bis(2-hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic acid, 3-[N-trishydroxymethylmethylamino]-2-hydroxypropanesulfonic acid, N-tris[hydroxymethyl]methyl-4-aminobutanesulfonic acid, 3-aminoadipic acid, aspartic acid, α -glutamic acid, β -glutamic acid, 1,3-diamino-2-hydroxypropane-N,N,N',N'- 25 tetraacetic acid, triethylenetetraaminehexaacetic acid, glucosamine, galactosamine, mannosamine, tris(hydroxymethyl)aminomethane, γ -carboxyglutamic acid, glucamine, glucosaminic acid, β -carboxyaspartic acid, α -hydroxymethylaspartic acid, tricine, 1,2,3,4-cyclopentanetetracarboxylic acid, 6-phosphogluconic acid, sorbitol, mannose, mannitol, mannonic acid, mannuronic acid, galactose, galactitol, galactaric acid, 30 galacturonic acid, fructose, sucrose, salts of any of the preceding moieties, and mixtures thereof.

Each A moiety has one or more functional groups. When the A moiety has one functional group, two or more A moieties are combined to provide for multiple functional groups in the oligomeric dispersant. When the A moiety has multiple functionalities, there is no requirement that more than one A moiety must be used.

- 5 Examples of the residue include, but are not limited to, hydroxyl, carboxylate, sulfate, sulfonate, sulfinate, phosphate, phosphonate, phosphinates, borate, boronate, boroxine, dioxaborolane, amine, quaternary ammonium, and mixtures thereof. The functional groups attach to the cement particle to be dispersed by adsorbing on to the cement particle. The more functional groups that are present on the A moiety, the more
- 10 strongly the A moiety can anchor to the cement particle.

Component B is an optional moiety, and if present, each B is independently a nonpolymeric moiety that is disposed between the A moiety and the C moiety, and is derived from a second component selected from the group consisting of C₁ to C₆ linear saturated hydrocarbons, C₁ to C₆ linear unsaturated hydrocarbons, C₁ to C₆ branched saturated hydrocarbons, C₁ to C₆ branched unsaturated hydrocarbons, C₆ to C₁₀ arylenes, nitrogen-containing compounds, and mixtures thereof. Nitrogen-containing compounds include, but are not limited to, any amine.

20 Illustrative examples of the B moiety include, but are not limited to, methylene, ethylene, n-propylene, n-butylene, n-pentylene, n-hexylene, isobutylene, neopentylene, propenylene, isobutenylene, diethylene triamine, triethylene tetramine, tetraethylene pentamine, or pentaethylene hexamine, phenylene, substituted arylenes such as



Each C component is at least one moiety that is a linear or branched water-soluble nonionic polymer substantially non-adsorbing to cement particles, and is preferably selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol),

30

monoaryloxy poly(oxyalkylene glycol), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof.

The C moiety has a number-average molecular weight from 500 to 100,000.
 5 Preferably, the C moiety has a number-average molecular weight from 1,000 to 50,000. Most preferably, the C moiety has a number-average molecular weight from 1,000 to 30,000.

The oligomeric dispersant of the present invention has number-average
 10 molecular weight from 650 to 100,000. Preferably, the dispersant has a number-average molecular weight from 1,150 to 50,000. Most preferably, the dispersant has a number-average molecular weight from 1,150 to 30,000.

For further clarification, A_x is preferably at least one of A-, A-A-, or A-A-A-;
 15

$B-(C)_z$ is preferably at least one of

$$B-C \quad B \begin{array}{l} \nearrow C \\ \searrow C \end{array} \quad B \begin{array}{l} \nearrow C \\ \rightarrow C \\ \searrow C \end{array} ; \text{ and}$$

$(A_x)_y-B$ is preferably at least one of

$$A_x-B \quad \begin{array}{c} A_x \nearrow B \\ A_x \searrow B \end{array} \quad \begin{array}{c} A_x \nearrow B \\ A_x \rightarrow B \\ A_x \searrow B \end{array} .$$

20

In another embodiment, the abovementioned composition of matter is incorporated into a cementitious formulation with a hydraulic cement. The oligomeric dispersant can be added as an admixture alone or in combination with other admixtures
 25 in the field, or it can be added to the cementitious formulation prior to delivery to the field.

The hydraulic cement comprising the cementitious formulation for which the dispersants are effective is selected from the group consisting of portland cement,

masonry cement, alumina cement, refractory cement, magnesia cement, calcium sulfoaluminate cement, and mixtures thereof.

Aggregate can be included in the cementitious formulation to provide for
5 mortars which include fine aggregate, and concretes which also include coarse aggregate. The fine aggregate are materials that pass through a Number 4 sieve (ASTM C125 and ASTM C33), such as silica sand. The coarse aggregate are materials that are retained on a Number 4 sieve (ASTM C125 and ASTM C33), such as silica, quartz, crushed round marble, glass spheres, granite, limestone, calcite, feldspar,
10 alluvial sands, or any other durable aggregate, and mixtures thereof.

Additionally, cement admixtures may be included in the cementitious formulation. Admixtures that can be added include, but are not limited to, set accelerators, set retarders, air-entraining agents, air-detraining agents, foaming agents,
15 defoaming agents, corrosion inhibitors, shrinkage-reducing agents, other known dispersing agents, pozzolans, pigments, and mixtures thereof.

The cementitious formulation may further comprise water. The water can be present in an amount from 20% to 100% based on the dry weight of the cement.
20

The dispersant of the present invention is generally present in the cementitious formulation in an amount from 0.005 to 2% based on the dry weight of the cement. Preferably, the dispersant is present in an amount from 0.01% to 1%.

25 An additive selected from the group consisting of soil, calcined clay, and mixtures thereof can be included in the cementitious formulation. The soil can be any soil including, but not limited to, fine sands, silty soils, and clay. The additive can replace up to 25% of the cement. Preferably, the additive replaces up to 20% of the cement.

30

In another embodiment of the present invention, there is provided a method of dispersing a cementitious formulation comprising a hydraulic cement in water,

including providing in said cementitious formulation the above-described oligomeric cement dispersant.

In another embodiment of the invention, an oligomeric dispersant wherein at least one A moiety in the oligomeric dispersant is blocked is used in combination with a second dispersant which is selected from another oligomeric dispersant of the present invention or any other suitable cementitious dispersant. By "blocked" it is meant that the residue on the A moiety does not interact with the cement until the residue is liberated. The residue is liberated/deblocked over time by hydrolyzing in the alkaline environment of the cementitious system. This provides for latent dispersant properties.

The effect of liberating over time results in a delay of dispersing performance that leads to extended slump retention performance. The residues on the A moiety that are blocked include, but are not limited to, trialkoxy silanes, triacyloxy silanes, and triaryloxy silanes. A preferred blocked residue is trialkoxy silanes.

The blocked oligomeric dispersant can be present in a cementitious formulation in an amount from 0.005 to 2% based on the dry weight of the cement. Preferably, the blocked oligomeric dispersant is present in an amount from 0.01% to 1%. Preferably, the ratio of the blocked oligomeric dispersant to the other dispersant is from 1:10 to 5:1. More preferably, the ratio is 1:5 to 3:1.

By any cementitious dispersant it is meant to include all chemicals that function as a dispersant, water-reducing agent, or plasticizer for cement. Illustrative examples include, but are not limited to, beta-naphthalene sulfonates, lignosulfonates, polyacrylic acids, polymethacrylic acids, polycarboxylates, and polyaspartates.

SPECIFIC EMBODIMENTS OF THE INVENTION

Oligomeric dispersants according to the present invention were synthesized and tested as described below. The molecular weights used herein are number-average molecular weights. The following tests were used: Slump (ASTM C143), Air content

(ASTM C231), and Set time (ASTM C403). Aggregates met the specifications of ASTM C33.

SYNTHESIS EXAMPLE 1

5 1.1g (0.003 mole) of 1,2,3,4,5,6-cyclohexane hexacarboxylic acid was suspended in 5.5g of deionized water. 6.52g of methoxy polyoxyalkylene amine (JEFFAMINE® M-2070 (XTJ-508) from Huntsman Corporation with a 2000 molecular weight) was slowly added to the mixture to achieve a homogeneous solution. 0.001g of 4-methoxy phenol was added while stirring the solution. The solution was heated to
10 180°C under nitrogen gas stream for 60 minutes. The reaction mixture was cooled to room temperature. The reaction product was dissolved in aqueous sodium hydroxide solution to obtain a 39.1 % solids solution at a pH 8.4.

SYNTHESIS EXAMPLE 2

15 0.57g (3.7 mmole) of 2-carboxyethylphosphonic acid was dissolved in 6g of water and 11.11g (3.7 mmole) of methoxypolyoxyalkylene amine (M3000 from BASF with a 3000 molecular weight) was added. The mixture was heated under nitrogen at 160°C for 4.5 hours.

SYNTHESIS EXAMPLE 3

20 2.44g of gluconic acid solution (48.2 % aqueous solution) was combined with 2g of deionized water in a 50ml round bottom flask. 6.12g of methoxy polyoxyalkylene amine (JEFFAMINE® M-1000 (XTJ-506) from Huntsman Corporation with a 1000 molecular weight) was added in portions while stirring. 0.002g of 4-methoxy phenol
25 was added. The solution was heated to 160°C under nitrogen stream for 90 minutes. The mixture was cooled to room temperature. The reaction mixture was dissolved in water to obtain a 40% solids solution at neutral pH.

SYNTHESIS EXAMPLE 4

30 A solution of 4.03g (16.3 mmol) of 3-(triethoxysilyl)propyl isocyanate in 20ml of tetrahydrofuran (THF) was added to 0.84g (8.15mmol) of diethylenetriamine in a flask cooled in an ice bath. The mixture was stirred at 0°C for 1 hour, then at ambient

temperature for 4 hours. The solvent was evaporated and the viscous, colorless product was dried in a vacuum.

0.848g (1.42 mmol) of the product was dissolved in 30ml THF. 2.92g (1.42 mmol) methoxy polyoxyethylene glycol-chloroformate, prepared from methoxy polyoxyethylene glycol (MPEG 2000 from Harcros Organics, Inc. with a 2000 molecular weight) and triphosgene, and 0.2ml triethylamine were added to the solution. The mixture was stirred at ambient temperature for 3 hours. The material was filtered and the solvent was evaporated. The resulting pale yellow solid was vacuum dried.

10

SYNTHESIS EXAMPLE 5

131.6g (0.048 equivalents of amine) of methoxy polyoxyalkylene amine (JEFFAMINE® XTJ-234 from Huntsman Corporation with a 3000 molecular weight) was combined with 10g (0.048 mole) of α -D-glucoheptonic- γ -lactone in an oven dried 250ml round bottom flask. The stirred mixture was heated to 110°C under a dry nitrogen gas purge for 5.5 hours.

EXAMPLE 1

Dispersants of the present invention were prepared and compared to dispersants of the prior art. For the A moiety, 1,2,3,4,5,6-cyclohexane hexacarboxylic acid was used in all samples for this example. For the C moiety, methoxy polyoxyalkylene amines were used. The following materials were used for the samples: Sample A, JEFFAMINE® M-1000 (XTJ-506) from Huntsman Corporation with a 1000 molecular weight; Sample B, JEFFAMINE® M-2070 (XTJ-508) from Huntsman Corporation with a 2000 molecular weight; Sample C, JEFFAMINE® XTJ-234 from Huntsman Corporation with a 3000 molecular weight; and sample D methoxy polyoxyethylene amine from Shearwater Polymers, Inc. with a 5000 molecular weight. Finally, a beta-naphthalene sulfonate-formaldehyde condensate (BNS) was tested as a comparison. The specific level of dispersant used is listed below in Table 1.

30

The water to cement ratio used was 0.35. The dispersant and water were hand mixed into 500g of Portland Type I cement and mixed to a uniform consistency. The

paste was then mechanically mixed at 700 rpm for one minute. The results of the testing are shown below in Table 1.

TABLE 1

Sample	Dose (% of cement)	Paste Mass Flow Rate (g/sec)	Paste Spread Diameter (cm)
A	0.2	109	12.6
B	0.2	66	11.0
C	0.2	59	10.7
D	0.2	53	10.6
BNS	0.2	17	0

The molecular weight of the "C" moiety of the oligomeric dispersants of the present invention did not influence the paste mass flow rate and the paste spread diameter. Compared to the BNS dispersants of the prior art, performance was improved.

EXAMPLE 2

The relationship between the number of attached C moieties on the A moiety and performance was tested. For the A moiety, 1,2,3,4,5,6-cyclohexane hexacarboxylic acid was used in all samples for this example. For the C moiety, a methoxy polyoxyalkylene amine, JEFFAMINE® M-1000 (XTJ-506) from Huntsman Corporation with a 1000 molecular weight was used. The molar ratio of the A moiety to the C moiety for the samples were: Sample A 1:1 (corresponding to general formula i, A_x-C; same sample from Example 1); Sample E 1:1.25, and Sample F 1:1.75 (E and F correspond to general formula iii, C-A_x-C). The prior art comparative example was the same as in Example 1. The samples were prepared as described above in Example 1. The results of the testing are shown below in Table 2.

TABLE 2

Sample	Dose (% of cement)	Paste Mass Flow Rate (g/sec)	Paste Spread Diameter (cm)
A	0.2	109	12.6
E	0.2	61	10.8
F	0.2	13	0
BNS	0.2	17	0

As shown in Table 2, as more C moieties are attached to the A moiety, the effectiveness as a dispersant decreases. As more C moieties are added, there are fewer functional groups with which to adsorb on to the particle to be dispersed. Anchor group binding strength is preferably balanced with the C moiety size and number for optimum performance.

10 EXAMPLE 3

The relationship of A moiety structure on dispersibility was tested at a higher water to cement ratio. Samples A, B, C, D, and F were prepared as described above. Sample G was prepared with 2-carboxyethylphosphonate as the A moiety with a methoxy polyoxyalkylene amine, JEFFAMINE® M-1000 (XTJ-506) from Huntsman Corporation with a 1000 molecular weight, as the C moiety. Also, the samples were compared to a plain paste without any dispersant, and a calcium lignosulfonate dispersant-containing sample was tested as a comparison. The water to cement ratio in this example was 0.42. The mix procedure was the same as in Example 1, except that each paste, except sample G, was stored for five minutes and then mechanically re-mixed for one minute at 700rpm. Sample G was mixed as in Example 1. The test results are shown in Table 3 below.

TABLE 3

Sample	Dose (% of cement)	Initial Paste Mass Flow Rate (g/sec)	Final Paste Mass Flow Rate (g/sec)	Initial Spread Diameter (cm)	Final Spread Diameter (cm)
Plain	---	60	29	9.7	7.8
A	0.1	128	101	13.0	12.2
F	0.1	116	73	12.1	11.4
B	0.1	133	90	13.0	12.3
C	0.1	121	91	12.6	11.2
D	0.1	122	79	12.6	11.2
G	0.2	75	51	10.9	10.4
Ca Ligno- sulfonate	0.19	86	44	11.0	9.6
BNS	0.1	80	33	10.5	8.6

The results in Table 3 show that the plain sample and the lignosulfonate sample
 5 lose about half of the flow in about 20 minutes. The BNS loses more than half of the
 initial flow. The dispersants of the present invention, however, lose less than half of
 the initial flow in the same time period. The dispersants of the present invention
 perform better than lignosulfonates at a lower dosage, perform better than BNS at the
 same dosage.

10

EXAMPLE 4

The relationship of dispersant structure, as influenced by C moiety molecular
 weight, to initial set time of a cement paste was tested. The dispersants tested were
 those from the previous examples. The water to cement ratio was 0.35. All
 15 dispersants were added at 0.2% based on the weight of cement. The mixing was the
 same as described above in Example 1. The initial set time was tested using a
 Form+Test automated set time apparatus using 300g of each prepared paste. The
 results are listed in Table 4 below.

TABLE 4

Sample	MW of C Moiety	Initial Set Time (hours)
A	1000	12.1
B	2000	10.2
C	3000	7.5
D	5000	6.1
Ca Lignosulfonate	N/A	6.5
BNS	N/A	4.9

N/A = not applicable

- 5 Table 4 shows that as the molecular weight of the C moiety increases, the initial set time is reduced.

EXAMPLE 4A

- The relationship of the number of attached C moieties on the A moiety in the dispersant structure to initial set time of a cement paste was tested. The dispersants are those from the previous examples. The water to cement ratio was 0.35. All dispersants were added at 0.2% based on the weight of cement. The mixing was the same as above Example 1. The initial set time was tested using a Form+Test automated set time apparatus using 300g of each prepared paste. The results are listed in Table 4A below.

TABLE 4A

Sample	Molar Ratio A moiety to C moiety	Initial Set Time (hours)
A	1:1	12.1
E	1:1.25	10.2
F	1:1.75	7.0
Ca Lignosulfonate	N/A	6.5
BNS	N/A	4.9

N/A = not applicable

- 20 The results in Table 4A show that as more C moieties are attached to the A moiety, the initial set time decreases.

EXAMPLE 5

The relationship of the A moiety functionality to fluidity of a cement paste was tested. The water to cement ratio was 0.35. The preparation of the paste samples was the same as in Example 3 above. The C moieties for the samples were methoxy polyoxyalkylene amine, JEFFAMINE® M-1000 (XTJ-506) from Huntsman Corporation with a 1000 molecular weight, for Samples 2-6, and methoxy polyoxyethylene glycol from Union Carbide Corporation with a 2000 molecular weight, for Sample 1.

TABLE 5

Sample	Starting A moiety	A Moiety Functionality after attachment to the C moiety	C Moiety MW	Number of A Moieties	Dose (% of cement)	Paste Mass Flow Rate (g/sec)	Paste Spread Diameter (cm)
1	succinic anhydride	1-COOH	2000	1	0.2	0	0
2	2-carboxyethyl phosphonic acid	1-PO ₃ H ₂	1000	1	0.3	7.9	0
3	citric acid	2-COOH 1-OH	1000	1	0.3	14	0
4	1,2,3,4,5,6-cyclohexane hexacarboxylic acid	5-COOH	1000	1	0.2	109	12.6
5	mellitic acid	5-COOH	1000	1	0.2	72	10.0
6	gluconic acid	5-OH	1000	1	0.2	62	12.7

10

The total number of active functional groups on the A moiety(s) influences the performance of the dispersant. As the total number of active functional groups increases, the dispersing performance increases.

15 **EXAMPLE 6**

The A moiety was varied to compare performance against prior art dispersants and a plain cement paste reference. The A moieties tested are listed below in Table 6. The C moiety was a methoxy polyoxyalkylene amine, JEFFAMINE® XTJ-234 from Huntsman Corporation with a 3000 molecular weight. The reference dispersant was a polymeric carboxylate backbone with polyether group side chains. The water to cement ratio was 0.35. The mix procedure was the same as in Example 1. The results are listed below in Table 6.

20

TABLE 6

Sample	Dose (% of cement)	Initial Paste Mass Flow Rate (g/sec)	Final Paste Mass Flow Rate (g/sec)	Initial Spread Diameter (cm)	Final Spread Diameter (cm)
Plain	--	0	0	0	0
Gluconate as "A"	0.2	66	53	14	14
Gluc- heptonate as "A"	0.15	95	85	19.5	19.5
Gluc- heptonate as "A"	0.1	71	58	14.7	14.5
Ca Ligno- sulfonate	0.3	5.6	0	0	0
BNS	0.3	81	25	10.7	7.3
Ref. Poly- carboxylate	0.1	110	73	16.7	16.0

The results in Table 6 show improved dispersant performance by the oligomeric dispersants over the calcium lignosulfonate and BNS dispersants, and comparable performance to the polymeric carboxylate/polyether dispersant. Also, glucoheptonate (with 6 hydroxyl groups) as the A moiety performs better than gluconate (with 5 hydroxyl groups) as the A moiety.

10 EXAMPLE 7

Several dispersants according to the present invention were compared to a plain sample and a calcium lignosulfonate dispersant in a concrete formulation. The A moiety was either gluconate or glucoheptonate. The C moiety was a methoxy polyoxyalkylene amine, being either JEFFAMINE® M-2070 (XTJ-508) from Huntsman Corporation with a 2000 molecular weight or JEFFAMINE® XTJ-234 from Huntsman Corporation with a 3000 molecular weight.

The plain mix consisted of 12.1kg of Portland cement, 37.8kg of crushed stone, 24.9kg of sand, and 6.65kg of water to provide a water to cement ratio of 0.55. The amount of dispersant is listed below in Table 7. The mixes were adjusted with sand and stone to compensate for the reduced water requirement with a dispersant to

maintain a constant concrete volume for all mixes. Dispersed mixes contained less water, as indicated by the % water reduction in Table 7.

The concrete mixer was loaded with a portion of the mix water. The dispersant, stone, cement and sand were added to the mixer. The mixer was started and the remaining water was added. The mixture was mixed for 5 minutes at a drum rotation rate of about 19 rpm. Note, mixes 3-6 contained a defoamer, which was a non-silicone proprietary mixture sold as SURFYNOL® DF-75 from Air Products, added at 0.75% by weight of the dispersant.

10

TABLE 7

Sample	Dose (%)	Water Reduction (%)	Slump (in)	% Air	Initial Set Time	Compressive Strength (Mpa)		
						1 day	11 days	28 days
Plain	--	--	7.5	0.8	5:08	1360	4200	4980
Calcium Lignosulfonate	0.2	8	7.75	1.4	6:51	1770	5550	6420
Gluconate/XTJ-508	0.2	10.4	7.75	4.4	7:01	1770	4970	5880
Gluconate/XTJ-234	0.2	10	7.5	2.1	6:17	1930	5030	6300
Glucoheptonate/XTJ-234	0.2	15.1	8	1.5	6:17	2600	6510	7410
Glucoheptonate/XTJ-508	0.2	16.8	8.25	1.6	6:48	2490	6800	7750

Oligomeric dispersant produces greater water reduction than lignosulfonate dispersants at the same dosage. Better performing oligomeric dispersants were less retarding with greater water reduction and produced higher concrete compressive strength. Glucoheptonate anchor performs better than the gluconate anchor.

EXAMPLE 8

A concrete batch was prepared to compare dispersants of the present invention to BNS and polycarboxylate dispersants. The dispersant of the present invention used a glucoheptonate molecule as the A moiety and as the C moiety, a methoxy polyoxyalkylene amine, namely JEFFAMINE® M-2070 (XTJ-508) from Huntsman Corporation with a 2000 molecular weight (2K), or JEFFAMINE® XTJ-234 from Huntsman Corporation with a 3000 molecular weight (3K). The reference dispersant was a polymeric carboxylate backbone with polyether group side chains.

The mix consisted of 20.5kg of Portland cement, 61kg of crushed stone, 46kg of sand, and 9.03kg of water to provide a water to cement ratio of 0.46. The amount of dispersant is listed below in Table 8.

5 The concrete mixer was loaded with a portion of the mix water. The dispersant, stone, cement and sand were added to the mixer. The mixer was started and the remaining water was added. The mixture was mixed for 5 minutes at a drum rotation rate of about 19 rpm. The slump and air were measured initially. The mixer rate was reduced to about 4 rpm until one minute before each sample time. At one
10 minute before taking the sample, the mixer rate was increased to about 19 rpm. Note, all mixes, except the BNS mix, contained a defoamer, which was a non-silicone proprietary mixture sold as SURFYNOL® DF-75 from Air Products, added at 0.75% by weight of the dispersant.

15 TABLE 8

Sample	Dose % cement	% Air			Slump (mm)			Set Time (hours)
		Initial	45 min	65 min	Initial	45 min	65 min	
Gluco.3k	0.2	1.4	1.9	2	230	170	115	6
BNS	0.4	2.2	1.7		215	70		5
Polycarboxylate	0.14	1.7	1.8	2.1	205	120	120	5
Polycarboxylate	0.16	1.1	2	2.1	230	180	165	5.75

The results in Table 8 show that the dispersant of the present invention has improved slump retention as compared to BNS, and performs comparably to the reference polycarboxylates to provide improved slump retention properties.

20

EXAMPLE 9

The alkoxysilane dispersant that was prepared as in Synthesis Example 4 was tested in combination with a polycarboxylate dispersant in a cementitious mixture. The polycarboxylate dispersant was a polymeric carboxylate backbone with polyether group
25 side chains. The cementitious formulation was prepared as described in Example 8. Both samples contained a defoamer, which was a non-silicone proprietary mixture sold as SURFYNOL® DF-75 from Air Products, added at 0.75% by weight of the dispersant. The results are reported in Table 9.

TABLE 9

Sample	Dose % cement	% Air			Slump (mm)			Set Time hours	Compressive Strength (psi)	
		Initial	65 min	125 min	Initial	65 min	125 min		1 day	7-day
Polycarboxylate	0.16	2.4	3.4	2.5	230	205	110	6.1	2660	5400
Polycarboxylate/ Alkoxy-silane	0.12/ 0.10	1.9	2.4	2.7	230	220	175	6.4	2690	5830

The alkoxy-silane dispersant improved concrete slump retention without increasing set time and decreasing early age concrete compressive strength.

5

EXAMPLE 10

The alkoxy-silane dispersant that was prepared as in Synthesis Example 4 was tested in combination with another oligomeric dispersant in a cementitious paste. The cementitious paste was prepared as described in Example 1 with a water to cement ratio of 0.35. The other oligomeric dispersant had glucoheptonate as the A moiety and JEFFAMINE® M-2070 (XTJ-508) from Huntsman Corporation with a 2000 molecular weight as the C moiety (Other). The alkoxy-silane "blocked" or latent dispersant was added at the dosages described below in Table 10.

15

TABLE 10

Dispersant	Dose % cement	Paste Mass Flow Rate (g/sec)				Paste Spread Diameter (cm)			
		Initial	60min	120min	180min	Initial	60min	120min	180min
Other	0.1	44	35	24	10	12.2	12.0	9.9	8.6
Other/ Alkoxy-silane	0.1	60	69	66	54	15.0	17.7	16.9	16.0
Other/ Alkoxy-silane	0.1	72	84	84	79	17.4	21.5	21.6	22.3
	0.2								

The results in Table 10 show that the alkoxy-silane dispersant significantly increases the duration of the dispersed state when used in combination with another oligomeric dispersant. The effect of the alkoxy-silane dispersant is related to dose, and it increases with increasing dose.

20

The present invention therefore is demonstrated to provide an oligomeric dispersant for dispersing cementitious particles, wherein the dispersant adsorbs on to the particle to be dispersed to provide a material that is several times more efficient than traditional dispersants, such as beta naphthalene sulfonates, sulfonated melamine
5 formaldehyde condensates, or calcium lignosulfonates, and to provide a full range (Type A to Type F) water reducing capability.

The present invention also includes the novel oligomeric dispersants which includes a molecule which is reaction product of component A, optionally component
10 B, and component C;

wherein each component A is independently a nonpolymeric, functional moiety that adsorbs on to a cementitious particle, and contains at least one residue derived from a first component selected from the group consisting of phosphates, phosphonates, phosphinates, hypophosphites, sulfates, sulfonates,
15 sulfates, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid esters, alcohols, carbohydrates, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, salts of any of the preceding moieties, and mixtures thereof;
20 thereof;

wherein component B is an optional moiety, where if present, each component B is independently a nonpolymeric moiety that is disposed between the component A moiety and the component C moiety, and is derived from a second component selected from the group consisting of linear saturated
25 hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, alicyclic hydrocarbons, aryl, phosphoester, nitrogen containing compounds, and mixtures thereof; and

wherein component C is at least one moiety that is a linear or branched water soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol),
30 poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy

poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof;

5 wherein if the A moiety contains any phosphate, phosphonate, phosphinate, or hypophosphite residue the molecule is further characterized by at least one of the following:

A) the molecule has a structure selected from the group consisting of:

- (i) A_x-C , (ii) A_x-C-A_x , (iii) $C-A_x-C$,
 (iv) $(C)_z-B-A_x-B-(C)_z$, (v) $(A_x)_y-B-C-B-(A_x)_y$, and mixtures thereof;

10 B) on any given A moiety there is more than one residue selected from the group consisting of phosphates, phosphonates, phosphinates, or hypophosphites; or salts thereof;

C) the molecule has a structure of $(A_x)_y-B-(C)_z$ with the proviso that the B moiety and the A moiety are not bound to each other through an alkylene amine linkage;

15 D) the C moiety is selected from the group consisting of poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides),
 20 polyoxazoles, and mixtures thereof;

wherein x is an integer from 1 to 3 and represents the number of independent A moieties, y is an integer from 1 to 3 and represents the number of independent chains of A moieties, and z is an integer from 1 to 3 and represents the number of independent C moieties;

25 as more fully described above.

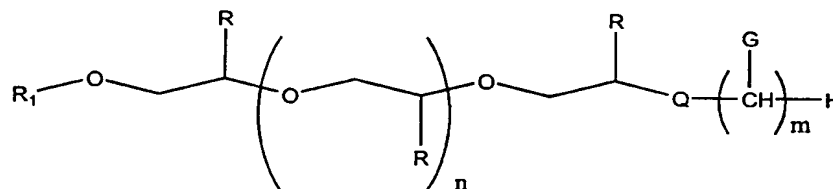
Preferably the molecule has a structure selected from the group consisting of

- (i) A_x-C ; (ii) A_x-C-A_x ; (iii) $C-A_x-C$;
 (iv) $(A_x)_y-B-(C)_z$; (v) $(C)_z-B-A_x-B-(C)_z$; (vi) $(A_x)_y-B-C-B-(A_x)_y$;

30 and mixtures thereof, wherein x is an integer from 1 to 3 and represents the number of independent A moieties, y is an integer from 1 to 3 and represents the number of A

moieties, and z is an integer from 1 to 3 and represents the number of independent C moieties.

Preferably, the molecule is represented by one of the following structures:



5

wherein R_1 is at least one of H, C_1 - C_{18} (preferably C_1 - C_6) alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

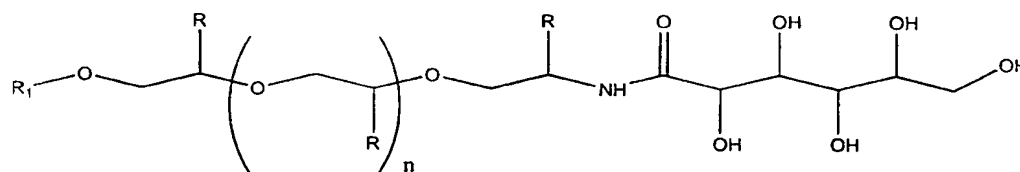
10

Q is at least one of carboxylic ester or amide

G is at least one of -OH, -COOH, a phosphate, a phosphonate, a phosphinate, a hypophosphite

$n = 10$ -500

$m = 5$ -7



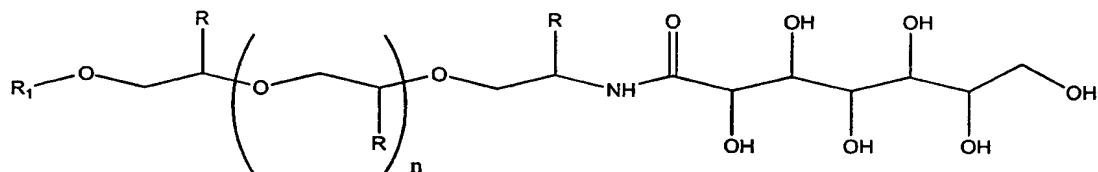
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wherein R_1 is at least one of H, C_1 - C_{18} (preferably C_1 - C_6) alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

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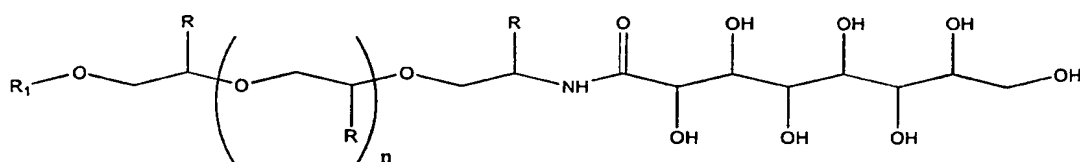
$n = 10$ -500



wherein R_1 is at least one of H, C_1 - C_{18} (preferably C_1 - C_6) alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

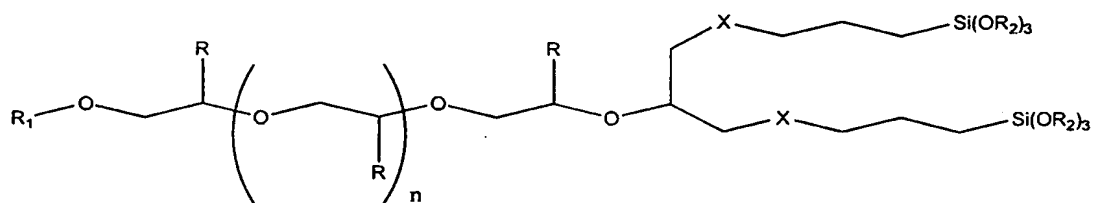
$n = 10$ -500



wherein R_1 is at least one of H, C_1 - C_{18} (preferably C_1 - C_6) alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

$n = 10$ -500



wherein R_1 is at least one of H, C_1 - C_{18} (preferably C_1 - C_6) alkyl, phenyl, benzyl, or alkyl sulfonate

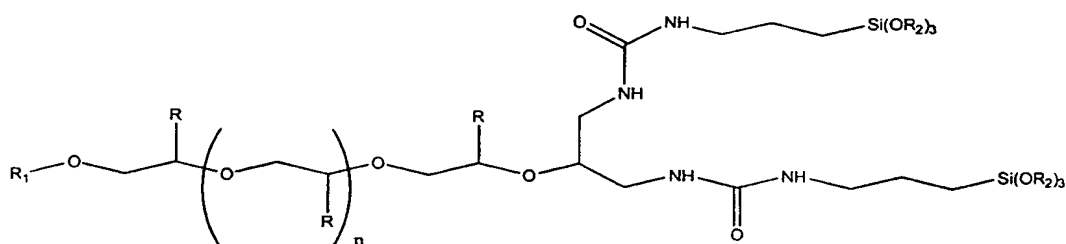
each R is independently at least one of H, methyl, ethyl, propyl, or styrene

each X is independently at least one of urea, carboxylic ester, or amide

R_2 is C_1 to C_6 alkyl

$n = 10-500$;

5 and



wherein R_1 is at least one of H, C_1-C_{18} (preferably C_1-C_6) alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

10

R_2 is C_1 to C_6 alkyl

$n = 10-500$

Naturally, more than one of such molecules may be used.

15

It should be appreciated that the present invention is not limited to the specific embodiments described above, but includes variations, modifications and equivalent embodiments defined by the following claims.

CLAIMS

1. A cementitious formulation comprising a cement and a dispersant comprising a reaction product of component A, optionally component B, and component C;
5 wherein each component A is independently a nonpolymeric, functional moiety capable of adsorbing on to a cementitious particle, and contains at least one residue derived from a first component selected from the group consisting of phosphates, phosphonates, phosphinates, hypophosphites, sulfates, sulfonates, sulfinates, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid esters, alcohols, carbohydrates, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, salts of any of the preceding moieties, and mixtures thereof;
10 wherein component B is an optional moiety, where if present, each component B is independently a nonpolymeric moiety that is disposed between the component A moiety and the component C moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, alicyclic hydrocarbons, aryl, phosphoester, nitrogen containing compounds, and mixtures thereof; and
15 wherein component C is at least one moiety that is a linear or branched water soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof;
20 wherein if the A moiety contains any phosphate, phosphonate, phosphinate, or hypophosphite residue the dispersant is further characterized by at least one of the following:
25
30

- A) the dispersant has a structure selected from the group consisting of:
 (i) A_x-C , (ii) A_x-C-A_x , (iii) $C-A_x-C$,
 (iv) $(C)_z-B-A_x-B-(C)_z$, (v) $(A_x)_y-B-C-B-(A_x)_y$, and mixtures thereof;
- 5 B) on any given A moiety there is more than one residue selected from the group consisting of phosphates, phosphonates, phosphinates, or hypophosphites; or salts thereof;
- C) the dispersant has a structure of $(A_x)_y-B-(C)_z$ with the proviso that the B moiety and the A moiety are not bound to each other through an alkylidene amine linkage
- 10 D) the C moiety is selected from the group consisting of poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof;
- 15 wherein x is an integer from 1 to 3 and represents the number of independent A moieties, y is an integer from 1 to 3 and represents the number of independent chains of A moieties, and z is an integer from 1 to 3 and represents the number of independent C moieties.
2. The cementitious formulation of claim 1, wherein the dispersant has a structure selected from the group consisting of
- 20 (i) A_x-C ; (ii) A_x-C-A_x ; (iii) $C-A_x-C$;
 (iv) $(A_x)_y-B-(C)_z$; (v) $(C)_z-B-A_x-B-(C)_z$; (vi) $(A_x)_y-B-C-B-(A_x)_y$;
 and mixtures thereof, wherein x is an integer from 1 to 3 and represents the number of independent A moieties, y is an integer from 1 to 3 and represents the number of A moieties, and z is an integer from 1 to 3 and represents the number of independent C moieties.
- 25 3. The cementitious formulation of claim 1, wherein the C moiety has a number average molecular weight from 500 to 100,000.

4. A cementitious formulation comprising a cement and a blocked oligomeric dispersant comprising a reaction product of component A, optionally component B, and component C;

5 wherein each component A is independently a blocked, nonpolymeric, functional moiety that adsorbs on to a cementitious particle after deblocking, and contains at least one residue derived from a first component selected from the group consisting of alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, salts of any of the preceding moieties, and mixtures thereof;

10 wherein component B is an optional moiety, where if present, each component B is independently a nonpolymeric moiety that is disposed between the component A moiety and the component C moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, aryl, phosphoester, nitrogen
15 containing compounds, and mixtures thereof;

wherein component C is at least one moiety that is a linear or branched water soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy
20 poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof; and

25 wherein the blocked oligomeric dispersant is present in the cementitious formulation in combination with a second dispersant selected from the group consisting of an oligomeric dispersant, a cementitious dispersant, and mixtures thereof;

wherein the oligomeric dispersant comprises a reaction product of component A1, optionally component B1, and component C1;

30 wherein each component A1 is independently a nonpolymeric, functional moiety that adsorbs on to a cementitious particle, and contains at least one residue derived from a first component selected from the group consisting of

phosphates, phosphonates, phosphinates, hypophosphites, sulfates, sulfonates, sulfinates, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid esters, alcohols, carbohydrates, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, salts of any of the preceding moieties, and mixtures thereof;

wherein component B1 is an optional moiety, where if present, each component B1 is independently a nonpolymeric moiety that is disposed between the component A1 moiety and the component C1 moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, alicyclic hydrocarbons, aryl, phosphoester, nitrogen containing compounds, and mixtures thereof; and

wherein component C1 is at least one moiety that is a linear or branched water soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol) poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof.

5. The cementitious formulation of claim 4, wherein the blocked oligomeric dispersant is present in an amount from 0.005% to 2% based on the weight of the cement.

6. The cementitious formulation of claim 4, wherein the ratio of blocked oligomeric dispersant to second dispersant is from 1:10 to 5:1.

7. A method of dispersing a cementitious formulation comprising a cement in water, comprising providing in said cementitious formulation the cement dispersant of claim 1 and mixing said cementitious formulation.

8. A method of dispersing a cementitious formulation comprising a hydraulic cement in water, comprising providing in said cementitious formulation a blocked oligomeric dispersant comprising a reaction product of component A, optionally component B, and component C;

5 wherein each component A is independently a blocked, nonpolymeric, functional moiety that adsorbs on to a cementitious particle, and contains at least one residue derived from a first component selected from the group consisting of alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, salts of any of the preceding moieties, and mixtures thereof;

10 wherein component B is an optional moiety, where if present, each component B is independently a nonpolymeric moiety that is disposed between the component A moiety and the component C moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, alicyclic hydrocarbons, aryl, phosphoester, nitrogen containing compounds, and mixtures thereof;

15 wherein component C is at least one moiety that is a linear or branched water soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof; and

25 wherein the blocked oligomeric dispersant is present in the cementitious formulation in combination with a second dispersant selected from the group consisting of an oligomeric dispersant, a cementitious dispersant, and mixtures thereof;

30 wherein the oligomeric dispersant comprises a reaction product of component A1, optionally component B1, and component C1;

 wherein each component A1 is independently a nonpolymeric, functional moiety that adsorbs on to a cementitious particle, and contains at least one

residue derived from a first component selected from the group consisting of phosphates, phosphonates, phosphinates, hypophosphites, sulfates, sulfonates, sulfinates, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid esters, alcohols, carbohydrates, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, salts of any of the preceding moieties, and mixtures thereof;

wherein component B1 is an optional moiety, where if present, each component B1 is independently a nonpolymeric moiety that is disposed between the component A1 moiety and the component C1 moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, alicyclic hydrocarbons, aryl, phosphoester, nitrogen containing compounds, and mixtures thereof; and

wherein component C1 is at least one moiety that is a linear or branched water soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol) poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof.

9. The method of claim 8, wherein the cementitious dispersant is selected from the group consisting of beta naphthalene sulfonates, lignosulfonates, polyacrylic acids, polymethacrylic acids, polycarboxylates, polyaspartates, and mixtures thereof.

10. A molecule comprising a reaction product of component A, optionally component B, and component C;

wherein each component A is independently a nonpolymeric, functional moiety that adsorbs on to a cementitious particle, and contains at least one

residue derived from a first component selected from the group consisting of phosphates, phosphonates, phosphinates, hypophosphites, sulfates, sulfonates, sulfinates, alkyl trialkoxy silanes, alkyl triacyloxy silanes, alkyl triaryloxy silanes, borates, boronates, boroxines, phosphoramides, amines, amides, quaternary ammonium groups, carboxylic acids, carboxylic acid esters, alcohols, carbohydrates, phosphate esters of sugars, borate esters of sugars, sulfate esters of sugars, salts of any of the preceding moieties, and mixtures thereof;

wherein component B is an optional moiety, where if present, each component B is independently a nonpolymeric moiety that is disposed between the component A moiety and the component C moiety, and is derived from a second component selected from the group consisting of linear saturated hydrocarbons, linear unsaturated hydrocarbons, saturated branched hydrocarbons, unsaturated branched hydrocarbons, aryl, phosphoester, nitrogen containing compounds, and mixtures thereof; and

wherein component C is at least one moiety that is a linear or branched water soluble, nonionic polymer substantially non-adsorbing to cement particles, and is selected from the group consisting of poly(oxyalkylene glycol), poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), monoalkoxy poly(oxyalkylene glycol), monoaryloxy poly(oxyalkylene glycol), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof

wherein if the A moiety contains any phosphate, phosphonate, phosphinate, or hypophosphite residue the molecule is further characterized by at least one of the following:

A) the molecule has a structure selected from the group consisting of:

- (i) A_x-C , (ii) A_x-C-A_x , (iii) $C-A_x-C$,
 (iv) $(C)_z-B-A_x-B-(C)_z$, (v) $(A_x)_y-B-C-B-(A_x)_y$, and mixtures thereof;

B) on any given A moiety there is more than one residue selected from the group consisting of phosphates, phosphonates, phosphinates, or hypophosphites; or salts thereof;

C) the molecule has a structure of $(A_x)_y-B-(C)_z$ with the proviso that the B moiety and the A moiety are not bound to each other through an alkylidene amine linkage;

5 D) the C moiety is selected from the group consisting of poly(oxyalkylene amine), poly(oxyalkylene diamine), monoalkoxy poly(oxyalkylene amine), monoaryloxy poly(oxyalkylene amine), poly(vinyl pyrrolidones), poly(methyl vinyl ethers), poly(ethylene imines), poly(acrylamides), polyoxazoles, and mixtures thereof;

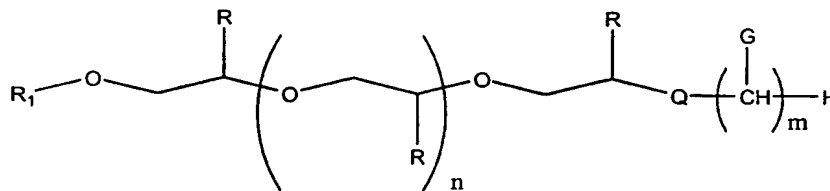
10 wherein x is an integer from 1 to 3 and represents the number of independent A moieties, y is an integer from 1 to 3 and represents the number of independent chains of A moieties, and z is an integer from 1 to 3 and represents the number of independent C moieties.

11. The molecule of claim 10, wherein the molecule has a structure selected from the group consisting of

15 (i) A_x-C ; (ii) A_x-C-A_x ; (iii) $C-A_x-C$;
(iv) $(A_x)_y-B-(C)_z$; (v) $(C)_z-B-A_x-B-(C)_z$; (vi) $(A_x)_y-B-C-B-(A_x)_y$;

and mixtures thereof, wherein x is an integer from 1 to 3 and represents the number of independent A moieties, y is an integer from 1 to 3 and represents the number of A moieties, and z is an integer from 1 to 3 and represents the number of independent C moieties.

12. The molecule of claim 10, wherein the molecule is represented by one of the following structures:



wherein R_1 is at least one of H, C_1-C_{18} alkyl, phenyl, benzyl, or alkyl sulfonate

25 each R is independently at least one of H, methyl, ethyl, propyl, or styrene

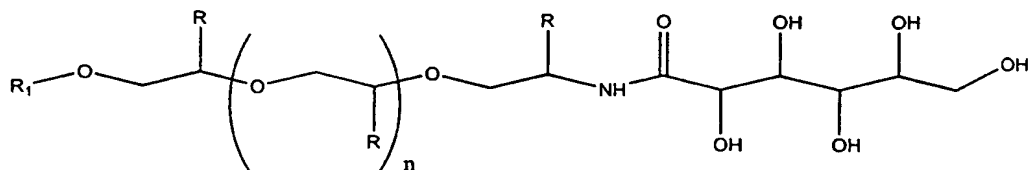
Q is at least one of carboxylic ester or amide

G is at least one of -OH, -COOH, a phosphate, a phosphonate, a phosphinate, a hypophosphite

$n = 10-500$

$m = 5-7$

5



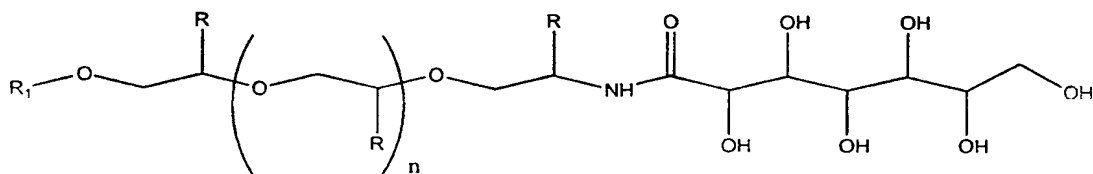
wherein

R_1 is at least one of H, C_1-C_{18} alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

10

$n = 10-500$



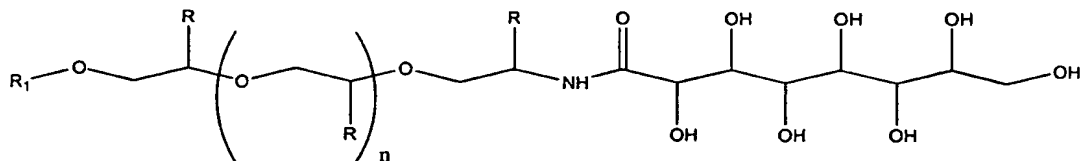
wherein

R_1 is at least one of H, C_1-C_{18} alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

15

$n = 10-500$

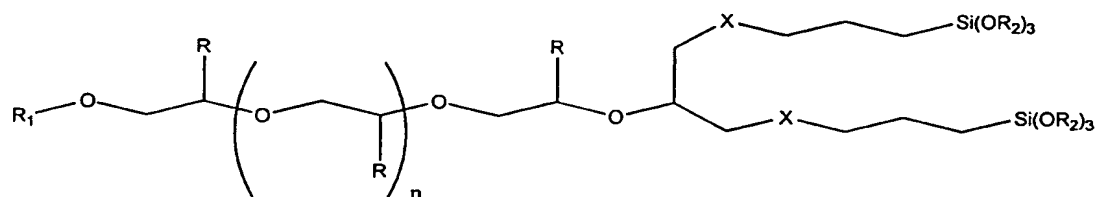


wherein

R_1 is at least one of H, C_1-C_{18} alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

$n = 10-500$



5 wherein R_1 is at least one of H, C_1-C_{18} alkyl, phenyl, benzyl, or alkyl sulfonate

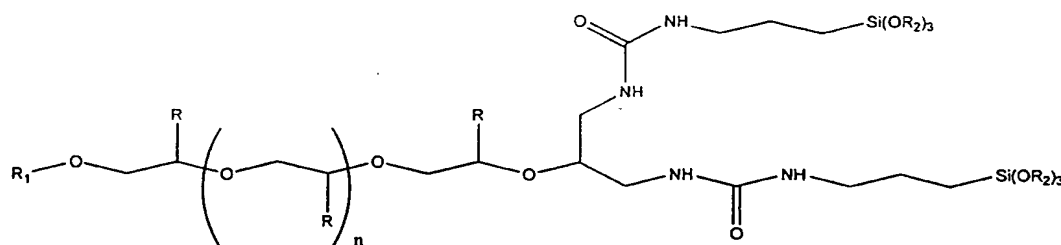
each R is independently at least one of H, methyl, ethyl, propyl, or styrene

10 each X is independently at least one of urea, carboxylic ester, or amide

R_2 is C_1 to C_6 alkyl

$n = 10-500$;

and



15 wherein R_1 is at least one of H, C_1-C_{18} alkyl, phenyl, benzyl, or alkyl sulfonate

each R is independently at least one of H, methyl, ethyl, propyl, or styrene

R_2 is C_1 to C_6 alkyl

20 $n = 10-500$

PCT/EP 00/06356

According to International Patent Classification (IPC) or to both national classification and IPC

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 879 445 A (GUICQUERO JEAN-PIERRE ET AL) 9 March 1999 (1999-03-09) claims 1,20 example 3	1-3,7, 10,11
X	EP 0 271 435 A (GRACE W R & CO) 15 June 1988 (1988-06-15) claim 1; example 1	1,3,7,10
E	WO 00 44487 A (JACHIMOWICZ FELEK ;CHUN BYONG WA (US); CLARK GINEVRA (US); WESTGAT) 3 August 2000 (2000-08-03) example 1 page 9, line 1 - line 25	1-3,7, 10-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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- **X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- ***** document member of the same patent family

Date of the actual completion of the international search

8 November 2000

Date of mailing of the international search report

08. 12. 2000

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Authorized officer

O'Sullivan, T

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/06356

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 803 521 A (NIPPON CATALYTIC CHEM IND) 29 October 1997 (1997-10-29) claim 19 examples A1-A5, B1, B2	1, 3, 7, 10
X	CHEMICAL ABSTRACTS, vol. 102, no. 18, May 1985 (1985-05) Columbus, Ohio, US; abstract no. 153885s, SANYO CHEM: "Agents for white-spot prevention on cement products " page 288; XP002152288 abstract & JP 59 164660 A (SANYO CHEM. IND.) 17 September 1984 (1984-09-17)	1-3, 7, 10
A	CHEMICAL ABSTRACTS, vol. 88, no. 58, 1978 Columbus, Ohio, US; abstract no. 93900y, YAMAMOTO ET AL: "Cement additive " page 93907; XP002152289 abstract & JP 07 776327 A (TAKEMOTO OIL AND FAT CO.) 27 June 1977 (1977-06-27)	1-12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 00/06356

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-12(in part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-12(in part)

Present claims 1-12. relate to an extremely large number of possible compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely to the polyether derivatives described by the present examples and their use in cementitious dispersions.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/06356

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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INTERNATIONAL SEARCH REPORT

International application No. **PCT/JP2004/011502**

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁷ C08G59/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl.⁷ C08G59/00-59/72

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	JP 2004-292737 A (Asahi Denka Kogyo Kabushiki Kaisha), 21 October, 2004 (21.10.04), Full text (Family: none)	1-9
A	JP 2002-338787 A (Zaidan Hojin Kawamura Rikagaku Kenkyusho), 27 November, 2002 (27.11.02), Full text (Family: none)	1-16
A	JP 2003-201335 A (Zaidan Hojin Kawamura Rikagaku Kenkyusho), 18 July, 2003 (18.07.03), Full text (Family: none)	1-16

☐ Further documents are listed in the continuation of Box C.

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Date of the actual completion of the international search
09 November, 2004 (09.11.04)

Date of mailing of the international search report
07 December, 2004 (07.12.04)

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